

complexes in the membrane to linear aggregates. The calculated values for the absorption, emission and lifetime using a model developed from *J* aggregate theory are consistent with the experimentally determined spectroscopic values, further proving a *J* type aggregation of the LH2 complexes in the photosynthetic membrane.

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Maximal Coherence at Room Temperature in the Bacterial Photosynthetic Reaction Center

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The earliest steps in bacterial photosynthesis require that an antenna system efficiently capture incident photons and shuttle the excitation energy to the “special pair” bacteriochlorophylls within the membrane-bound reaction center where charge separation occurs. Previous work has shown coherent energy transfer - a wavelike transfer process - among peripheral chromophores, bacteriopheophytins and accessory bacteriochlorophylls, at cryogenic temperatures. Whether or not this coherent transfer extends to the special pair, however, has remained elusive at any temperature. Here we report direct evidence that the special pair is coherently coupled to the accessory bacteriochlorophylls and that this coherence dephases only upon transfer to the special pair - the maximal amount of coherence physically possible. We employ Gradient Assisted Photon Echo Spectroscopy to simultaneously excite the bacteriopheophytins, accessory bacteriochlorophylls and the special pair in the reaction center from *Rhodospirillum rubrum*. These results suggest the bacteria exploits coherent energy transfer at room temperature.

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Efficient Intrinsic Photoprotection in Strongly Coupled (Bacterio) Chlorophyll Complexes

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Chlorophyll (Chl) molecules in photosynthetic proteins are known to produce highly toxic singlet oxygen under illumination as a result of energy transfer from their triplet excited states to oxygen. To prevent the formation of singlet oxygen, carotenoids (Car) are typically positioned close to Chl to ensure rapid triplet-triplet energy transfer from Chl to Car, which can then safely dissipate the energy of the excited states. Our recent studies revealed a new, unconventional, but very efficient photoprotection mechanism in strongly coupled natural and artificial light-harvesting complexes that does not rely on the presence of carotenoids. Experimental studies on carotenoid-free chlorosomes and artificial bacteriochlorophyll (BChl) aggregates show that these structures are at least three orders of magnitude more stable to photodamage than monomeric forms of BChl. It was proposed that this photoprotection in strongly coupled arrays of pigments is due to triplet exciton formation, which lowers the energy of the triplet exciton substantially below that of singlet oxygen.

In this report we present the results of our ongoing comprehensive study of the properties of triplet excited states of monomeric BChls, Chl aggregates and chlorosomes by means of EPR, time-resolved optical pump-probe spectroscopy and steady-state IR phosphorescence spectroscopy.

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Computational Modeling of Excitation Energy Transfer in Xanthorhodopsin, a Model Light-Harvesting System

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Xanthorhodopsin (xR), a light-driven proton pump, is unique among the rhodopsin family because it contains not one, but two strongly interacting chromophores, the retinal and a carotenoid. The carotenoid is bound to the protein and acts as a light-harvesting antenna, transferring energy to the retinal with ~40% quantum efficiency (Balashov et al., *Science* **309**, 2005). Unlike photosynthetic complexes in which excitation energy transfer (EET) occurs from a large collection of antennas to a reaction center, the EET in xR occurs directly between the retinal and a single bound carotenoid. Thus, xR serves as

a simple (and computationally accessible, albeit challenging) model system for understanding EET in light-harvesting systems. Here, we present the results of long (aggregate length > 350 ns) classical molecular dynamics (MD) simulations, starting from the x-ray crystal structure of xR (Luecke et al., *PNAS* **105**, 2008), coupled with single-point quantum mechanical (DFT) calculations performed on hundreds of simulation snapshots, to address two points. First, because the resolution of the crystal structure is not sufficiently high to resolve protons, the protonation state of the counterion complex (specifically, the His62-Asp96 pair) is unknown, so we ran four MD simulations in parallel, each with a different combination of protonation states for the His-Asp pair. The MD simulations, as well as DFT calculations of the retinal excited state energies, identify a single state that is most consistent with experimental data. Second, we probe the effects of small structural changes, which occur within the context of a thermally disordered lipid (POPC) bilayer, on the retinal excitation energies, and we conclude that the environment could play an important role in the EET between the bound carotenoid and the retinal.

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Structural Dynamics in Chloroplast Signal Recognition Particle (cpSRP) Proteins Studied with Single Molecule Fluorescence

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The interdomain structural dynamics of cpSRP43 protein interacting with cpSRP54 protein is studied by single molecule FRET, FCS, and ensemble fluorescence spectroscopy in order to understand the protein-protein interactions that help to transport LHCP into the thylakoid membrane for photosynthesis. Several double Cys and single Cys mutants of cpSRP43 and cpSRP54 proteins are cloned, expressed, purified and then specifically labeled with fluorescent dyes. The single molecule FRET and FCS equilibrium binding results suggest that the fluorescence labeling does not affect the cpSRP43-cpSRP54 interaction. Furthermore, we find that cpSRP43 proteins are very heterogeneous in structure and that cpSRP43 proteins undergo complex interdomain structural dynamics when interacting with cpSRP54 protein.

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Kinetic Model for Assessing the Effect of pH-Dependent Nonphotochemical Quenching of Chlorophyll Excitations on the Energetic Output of Chloroplasts

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The controlled dissipation of chlorophyll excitations protects photosynthetic organisms from inhibition of photosystem II. This dissipation, commonly known as nonphotochemical quenching (NPQ), enhances plants' fitness in natural conditions where sunlight intensity fluctuates. To identify the properties of feedback loop(s) controlling NPQ that enable it to effectively balance light harvesting and photoprotection, we have developed a mathematical model of photosystem II that incorporates molecular mechanisms for nonphotochemical quenching containing the PsbS protein and the xanthophyll cycle. The model accurately reproduces measurements of chlorophyll fluorescence over several minutes in intact leaves of the plant *Arabidopsis thaliana*. The model enables calculation of the effect of NPQ on both photoinhibition and energy consumption by the carbon reactions. This calculation provides a framework for quantifying the role of feedback-regulated photoprotection in enhancing the ability of plants to thrive in variable light conditions. Because the model incorporates mechanistic details, it has the potential to inform on modifications to improve the feedback loop controlling rapid nonphotochemical quenching to optimize the role of PSII regulation in maximizing biomass production.

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Measurement of the Microscopic Dynamics of Photoprotection in Living Cells of Green Algae

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Photosynthetic organisms reduce inhibition of photosystem II (PSII) in variable light conditions by using a suite of photoprotective mechanisms called